METHOD FOR FABRICATING COMPOSITE MATERIALS AND REPRESENTATIVES OF SUCH COMPOSITE MATERIALS

Background of the Invention

FIELD OF THE INVENTION

The present invention relates to a method for fabricating a composite material out of a parent substance containing silicon nitride and a metal silicide, through gas pressure sintering in a nitrogenous atmosphere and a silicon-containing composite material, whose silicon-containing constituents are made of Si_3N_4 and of a metal silicide.

BACKGROUND INFORMATION

~~Composite~~ there are composite materials, which contain silicon nitride and metal silicide, and methods for their preparation ~~are generally known~~. The fabrication of such materials through single-axial ~~hot-pressing (unconfined sintering under pressure) is described in German patents DE 37 34 274 C2 and DE 36 06 403 C2, the parent substance containing Si_3N_4 and, as silicide, $MoSi_2$, and in the EP 0 335 382 A1, the parent substance containing Si_3N_4, Mo_5Si_3 as silicide~~ and carbon, and the fabricated material ~~containing~~ contains as metal silicide, Mo_5Si_3C or, more precisely, $Mo_{5-X}Si_3C_{1-Y}$ ($0 \le X \le 2$; $0 \le Y \le 1$). The electrical properties of the materials fabricated in this manner are able to be selectively adjusted. It is believed that the ~~The~~ method is industrial and requires considerable outlay for energy consumption and that the ~~The~~ application of the method only permits fabrication of complex geometrical structures in expensive, hard-machining operations.

~~German Patent DE 195 00 832 A1, i.e., European Patent EP 0 721 925 A2 discuss the~~ fabrication of highly heat-resistant silicon nitride composite materials, which contain a reinforcement component of Me_5Si_3 and, moreover, $MeSi_2$ or $MeSi_2$, and silicides of other stoichiometries, Me standing for metal. Mixed into the parent substance as metal silicide are $MeSi_2$ and Me_5Si_3, or only $MeSi_2$. The metals ~~are preferably~~ may be selected from the group including molybdenum, tungsten, chromium, tantalum, niobium, manganese and vanadium. The sintering is performed as gas pressure sintering (at N_2 pressures of 100 bar), which makes it possible to fabricate molded articles (shaped bodies), virtually with their final contours, in ceramic injection molding or pressing processes, with subsequent green processing, or in hot-pressing (sintering under pressure) processes. Special electrical properties cannot be

~~adjusted.~~

The Present Invention and Advantages Thereof

SUMMARY OF THE INVENTION

AN Object of an exemplary embodiment of ~~The object of~~ the present invention is an industrially simple and energy-saving method for fabricating composite materials containing silicon nitride and metal silicide and having fixed electrical properties, which makes it possible to manufacture the molded articles, virtually with their final contours, from the composite material, prior to the sintering operation, and to specify representatives of such composite materials.

~~This objective is achieved by a method of the type mentioned at the outset, where Me_5Si_3 is~~ introduced as the metal silicide into the parent substance, the partial pressure of the nitrogen being established as a function of the sintering temperature in such a way that, at the lower limit of the practical range, Si_3N_4 is still thermodynamically stable and, at the upper limit, Me_5Si_3, and is dissolved into a composite material of the type mentioned at the outset, the metal silicide being selected from the group Nb_5Si_3, V_5Si_3, Ta_5Si_3 and W_5Si_3.

TO

~~The inventors discovered a way to~~ exploit the advantages of the gas-pressure sintering method, at the same time while manufacturing composite materials having fixed electrical

it was

~~properties. They~~ ascertained that the electrical properties cannot be adjusted in a determinate fashion (definably) when N_2 partial pressures are applied above a specific pressure range.

it was found that there is

During test trials, ~~they found~~ a range of the N_2 partial pressures within which one can prevent other silicon-containing components, besides Si_3N_4 and Me_5Si_3, from being present in the ~~finished composite material. In this manner, they were able to fabricate composite materials~~ having fixed electrical properties. In comparison to the hot-pressing (sintering under pressure) method, the gas-pressure sintering method makes do with a much simpler sintering

exemplary method

device. Compact, high-strength materials are able to be fabricated with the ~~method~~ according to the present invention. In comparison to materials containing $MeSi_2$, materials containing

are believed to

Me_5Si_3 ~~exhibit~~ a very low temperature dependency of the electrical conductivity.

The

It ~~is not critical when the~~ method is carried out in such a way that the metal silicide in the composite material has a carbon concentration (preferably between about 0.3 and about 0.6 %

by weight specific to the composite material), i.e., is present as $Me_5Si_3(C)$.

Further advantageous refinements of the method according to the present invention and of the composite materials according to the present invention are delineated in the dependent claims.

Drawing

In the following, the present invention is elucidated on the basis of exemplary embodiments illustrated in the drawing, whose figures show:

Figure 1 plotted in a diagram over the sintering temperature, the logarithm of the lower and upper limit values of the N_2 partial pressures, applicable in the method according to the present invention, for fabricating a composite material containing Mo_5Si_3; and

Figure 2 the same as in Figure 1, however, for fabricating a composite material containing Nb_5Si_3.

DETAILED DESCRIPTION

The exemplary embodiments of the method according the present invention described in the following are believed to be ~~in fact~~, particularly advantageous. However, they are merely provided by way of example, and ~~many~~ suitable appropriate variations are possible, without departing from the scope of the claims.

To fabricate the composite materials, a preconditioned Si_3N_4 powder is first mixed with sinter additives, such as Al_2O_3, Y_2O_3, or the like, which ~~in~~ in terms of the entire inorganic concentration -, make up less than about 10% by weight, Me_5Si_3 in suitable percentages by weight and, in some instances, organic pressing and/or binding agents, with the addition of an organic solvent - preferably - in an attritor mill. The attrited suspension is dried, for example, in a rotary evaporator. From the dried powder, through cold-isostatic pressing at pressures of between about 150 and 250 MPa, molded articles are produced, which, subsequent to the pressing operation, can obtain their final shape in a green processing. Other processing possibilities following the introduction of appropriate binding agents, include ceramic

injection molding (CIM) or extrusion. For debinding and/or presintering purposes, the molded articles are treated at approximately 600°C under a pressure of 1 bar in an inert gas atmosphere for about two hours, the organic constituents being removed, virtually without leaving any residues. The main sintering operation then follows, ~~preferably~~ in a gas-pressure sintering furnace at a temperature within a range of about 1700 and 1900°C, ~~and preferably~~ between about 1800 and 1900°C, under a defined partial N_2 pressure (total pressure between about 0.1 MPa and 10 MPa), which is set so as to achieve thermodynamic equilibrium of the Si_3N_4 phase and the Me_5Si_3 or $Me_5Si_3(C)$ phase during the sintering compression, i.e., to ensure they do not enter into any chemical reactions. The usable range of the partial N_2 pressure at a specific temperature is dependent upon the metal silicide. In the diagrams of Figures 1 and 2, the ranges of the usable partial N_2 pressures, measured in bar, (p_{N2}) for mixtures containing Mo_5Si_3 or Nb_5Si_3 are plotted as $\log(p_{N2}\ [\text{bar}])$ as a function of the temperature. In each case, the upper and lower limiting curves satisfy, for Mo-containing mixtures, the equations

$$y_1 = 5.3071 \cdot \ln(T) - 37.014$$

respectively

$$y_2 = 7.3494 \cdot \ln(T) - 54.124$$

and, for Nb-containing mixtures, the equations

$$y_1 = 7.8968 \cdot \ln(T) - 58.8$$

respectively

$$y_2 = 8.2598 \cdot \ln(T) - 62.064,$$

y_1 and y_2 representing $\lg(p_{N2}\ [\text{bar}])$ values. Below the limited range, Si_3N_4 reacts with Me_5Si_3. Above the limited range, Me_5Si_3 reacts with nitrogen. The curves were determined in serial investigations, in that, at a fixed temperature of between about 1700 and 1900°C, the partial N_2 pressures were determined at which Me_5Si_3 and Si_3N_4 are thermodynamically stable. The criterion that no reaction took place is, in each case, that only the desired silicon-containing phases are found in the X-ray diffractogram of the sintered material. The equations named above were then determined on the basis of these values, of known data, such as enthalpies of formation, and of thermodynamic functions. The sintering process takes about two to five hours.

The specific electrical resistance of the composite materials fabricated in accordance ~~with the~~ present invention is adjusted through the selection of the metal in the silicide and the concentration and the distribution of the silicide in the composite material. Beyond the particular percolation range, specific electrical resistances of between about $1.7 \cdot 10^{-4}\Omega$cm and $1 \cdot 10^{12}\Omega$cm can be reproducibly adjusted with materials containing $Nb_5Si_3(C)$, and of between about $1 \cdot 10^{-5}\Omega$cm and $1 \cdot 10^{12}\Omega$cm with materials containing $Mo_5Si_3(C)$. The specific resistance is measured using the four-point method.

Using qualitative and quantitative chemical and physico-chemical analyses and radiographic phase analysis, one can verify that - apart from the carbon concentration and without consideration of the organic constituents - the sintered materials have the same composition as the mixture that the fabrication process originated with. During the sintering process in a graphite furnace, the carbon ~~is preferably~~ contained in the metal silicide with a concentration, in terms of the composite material, of between about 0.3 and 0.6 % by weight, and ~~quite preferably~~ with about 0.5 % by weight. The room (ambient) temperature stabilities of the composite materials do not lie under 500 MPa.

Besides standing for niobium and molybdenum having comparable results for all metals of the 5th and 6th subgroup of the periodic ~~system~~, Me can stand, in particular, for vanadium, tantalum, chromium and tungsten.

The ~~method~~ of the present invention is described in greater detail in the following on the basis of two special examples.

Example 1

The parent substance was mixed from 36 % by weight of Si_3N_4, 1.7 % by weight of Al_2O_3, 2.38 % by weight of Y_2O_3, 60 Nb_5Si_3 % by weight and the usual pressing and/or binding agents. The average particle size of the Si_3N_4 was 0.7 μm, and that of the Nb_5Si_3 0.7 μm. The cold isostatic compression at 200 MPa was followed by a pre-sintering under an inert gas at up to 600°C, argon being used (nitrogen also could have been used). Sintering subsequently took place at a partial N_2 pressure of 0.5 MPa (total pressure 1 MPa) and 1800°C in a

graphite furnace.

The density of the composite material obtained was 97% of the material density. The radiographic phase analysis performed after the sintering process yielded exclusively Si_3N_4 and $Nb_5Si_3(C)$ as silicon-containing phases. As a specific electrical resistance, $3 \cdot 6 \cdot 10^{-3} \Omega cm$ was determined at 25 °C. The temperature coefficient of the specific electrical resistance amounted to $2 \cdot 10^{-4} K^{-1}$.

Example 2

Besides the fact

~~Besides~~ that the inorganic constituents of the parent substance were made up of 54 % by weight of Si_3N_4, 2.6 % by weight of Al_2O_3, 3.4 % by weight of Y_2O_3, 40 Nb_5Si_3 % by weight, the method was carried out in the same manner as in Example 1.

The analyses performed on the sintered material likewise yielded the attained material density amount of 97%, the radiographic phase analysis yielded exclusively Si_3N_4 and $Nb_5Si_3(C)$ as silicon-containing phases, and $2 \cdot 10^2 \Omega cm$ at 25 °C was determined as a specific electrical resistance.